Abstract:

Tandem Catalyis: Dehydrogenation and Hydrogenation

Co-supervisor 1: Prof. Dr. Kallol Ray, HU Berlin

Co-supervisor 2: Prof. Dr. Martin Kaupp, TU Berlin

The research proposal discusses a strategy to perform tandem catalysis (hydrogen production along with hydrogenation of carbon dioxide) by using a heterobimetallic catalyst. Although efficient methanol dehydrogenation is well documented in the literature, the release of harmful carbon dioxide gas as a by-product remains a concern. The present proposal postulates a bimetallic catalyst with ruthenium and cobalt active sites connected through a linking group. Whereas the ruthenium centre would engage in the methanol dehydrogenation, the released CO_2 and H_2 (one mole) would travel to the cobalt site where CO_2, the gas of global concern, would get hydrogenated. In this manner, a formate salt and two moles of hydrogen (a promising source of energy) per cycle shall be the product of the overall reaction.

Extended description version of the project:

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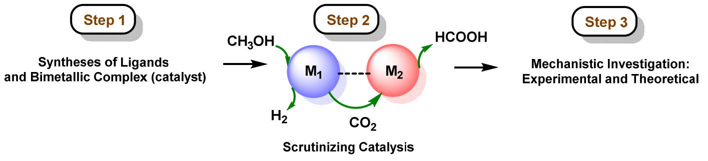
1. State of the art and overall goal of the project



Scheme 1

Hydrogen gas is flammable and can diffuse through various metals. Accordingly, its storage and transportation are extremely challenging. Methanol can be used as an alternate source of hydrogen. Methanol is liquid at room temperature facilitating easy handling, storage and transportation. It is an acclaimed source of hydrogen as it contains 12.6% hydrogen by weight. Seminal contributions by Beller and co-workers have recently described the use of a monomeric ruthenium pincer complex in the efficient dehydrogenation of methanol to liberate three molecules of hydrogen and one molecule of unfavourable carbon dioxide.[1] In the present proposal, we seek to sequester the CO_2 released from the reaction by converting it into a valuable chemical by a subsequent hydrogenation reaction in a single pot reactor. The project aims to (i) synthesize bimetallic complexes that would serve as active sites to perform two mechanistically different reactions; (ii) employ the catalyst to perform dehydrogenation and hydrogenation reactions and (iii) decipher and establish the underlining mechanism involved in the process. The proposed ligand design to achieve a single bimetallic catalyst over two individual catalysts would decrease the operating distance between the two tandem catalytic sites and ensure the easy availability/transfer of the reactants. Here the expertise of the Ray group in dealing with the trapping, isolation and characterization of reactive intermediates[2] and of the Kaupp group to compute and analyze *NMR chemical shifts* of the paramagnetic reactive intermediates[3] will allow for the successful implementation of the research project. The three modules of the work plan may be pictographically depicted in Scheme 1

2. Specific aims and how they may be reached

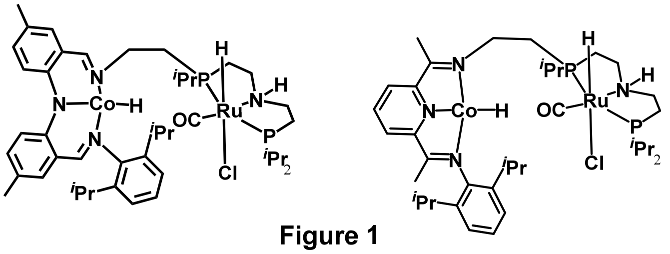


Figure 1

<u>Synthetic Outline:</u> The syntheses of the peripheral ligands and their chelations with the metals to obtain different bimetallic catalysts (Figure 1) would be the first step towards the dissemination of the proposed project. Pincer-type ligands are proposed at each metal centre that will provide chemical and thermal stability to the synthesized complex and prevent its dissociation under catalytic conditions. The iso-propyl groups are placed in the ligating frameworks to allow for steric stability. The ruthenium end of the catalyst design comprises of a secondary amide pincer ligand, which will ensure a typical Noyori

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[1] Nielsen, M., Alberico, E., Baumann, W., Drexler, H. –J., Hunge, H., Gladiali, S., Beller, M. *Nature* **2013**, *495*, 85.

[2] (a) P. Gerschel, BBattistella, D. Siegmund, K. Ray, U. P. Apfel, *Organometallics* **2020**, *39*, 1497; (b) P. Gerschel, K. Warm,E. R. Farquhar, U. Englert, M. L. Reback, D. Siegmund, K. Ray, U.-P. Apfel, *Dalton Trans.* **2019**, *48*, 5923; (c) X. Engelmann, D. D. Malik, T. Corona, K. Warm, E. R. Farquhar, M. Swart, W. Nam, **K. Ray**, *Angew. Chem. Int. Ed.* **2019**, 58, 4012.

[3] (a) A. Bertarello, L. Benda, K. J. Sanders, A. J. Pell, M. J. Knight, V. Pelmenschikov, L. Gonnelli, I. C. Felli, M. Kaupp, L. Emsley, R. Pierattelli, G. Pintacuda *J. Am. Chem. Soc.* **2020**, *142*, 16757; (b) L. Benda, J. Mareš, E. Ravera, G. Parigi, C. Luchinat, M. Kaupp, J. Vaara *Angew. Chem., Int. Ed. Engl.* **2016**, *55*, 14713.

type catalytic site to promote acceptorless methanol dehydrogenation. The precursors for the proposed ligand system are either commercially available or are easy to synthesize.

Probing catalytic activity towards tandem alcohol dehydrogenation and CO_2 hydrogenation: The heart of the proposed project would be to employ the designed heterometallic complex for the desired catalysis. Two independent but simultaneous catalytic reactions are expected at each metal centre. The ruthenium site is designed to perform acceptorless alcohol dehydrogenation (this has been established to furnish 3:1 molecules of H_2/CO_2); the CO_2 as the by-product of the reaction is expected to be hydrogenated at the cobalt center, in parallel. The bimetallic catalyst as depicted in Figure 2 will enter the catalytic cycle by dehydrochlorination of the ruthenium catalytic site upon its activation by a base. Notably, the reaction at the ruthenium center is expected to proceed through the well reported outer sphere mechanism that will involve a proton transfer to the amido ligand and a hydride transfer to the metal; the metal-ligand cooperativity at the ruthenium site would lead to the liberation of dihydrogen with the concomitant formation of formaldehyde. Subsequent reaction of formaldehyde with water will form gem-diol, which can be further dehydrogenated at the Ruthenium center to yield a second molecule of H_2 and formic acid. The dehydrogenation of formic acid will yield the third molecule of hydrogen and carbon dioxide. The released CO_2 would reach the Co site and would get inserted into the Co-H bond leading to the formation of formate, which can be precipitated out in presence of a base. The overall reaction may be summarized by equation 1:

$$CH_3OH \xrightarrow[2H_2]{[Ru],\ H_2O} H_2 + CO_2 \xrightarrow[\text{Base (eg. KOH)}]{[Co]} HCOOK + H_2O$$

equation 1

Rapid freeze quench techniques will be employed to trap the various reactive intermediates in the reaction in order to establish the reaction mechanism. Characterizations will be performed by cryo electro-spray mass spectroscopy, low temperature UV/Vis and NMR measurements, as well as by X ray absorption spectroscopy. The spectroscopic data gathered will be used as a basis for evaluating density functional theory (DFT) computations used to generate quantitative bonding descriptions and reaction trajectories, which will reinforce experimentally gathered information and provide insights into reactivity.

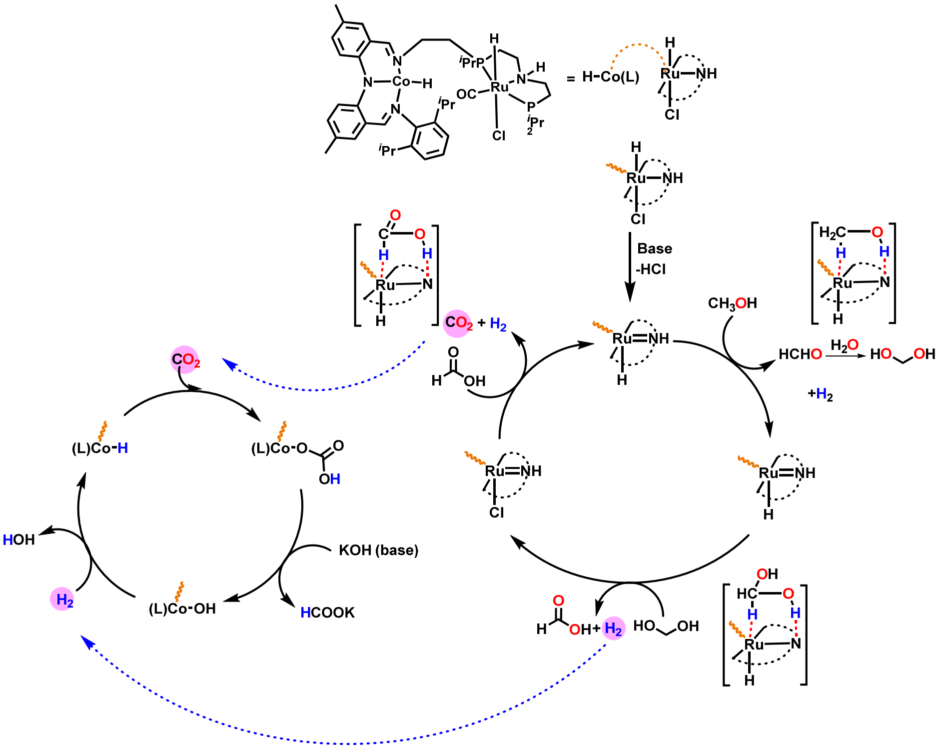

Figure 2